

Invariant Form of Hyperfine Interaction with Multipolar Moments - Observation of Octupolar Moments in NpO_2 and CeB_6 by NMR -

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The invariant form of the hyperfine interaction between multipolar moments and the nuclear spin is derived, and applied to discuss possibilities to identify the antiferro-octupolar (AFO) moments by NMR experiments. The ordered phase of NpO_2 and the phase IV of $\text{Ce}_{1-x}\text{La}_x\text{B}_6$ are studied in detail. Recent ^{17}O NMR for polycrystalline samples of NpO_2 are discussed theoretically from our formulation. The observed feature of the splitting of ^{17}O NMR spectrum into a sharp line and a broad line, their intensity ratio, and the magnetic field dependence of the shift and of the width can be consistently explained on the basis of the triple \mathbf{q} AFO ordering model proposed by Paixão *et. al.* Thus, the present theory shows that the ^{17}O NMR spectrum gives a strong support to the model. The 4 O sites in the fcc NpO_2 become inequivalent due to the secondary triple \mathbf{q} ordering of AF-quadrupoles: one cubic and three non-cubic sites. It turns out that the hyperfine field due to the antiferro-dipole and AFO moments induced by the magnetic field, and the quadrupolar field at non-cubic sites are key ingredients to understand the observed spectrum. The controversial problem of the nature of phase IV in $\text{Ce}_{1-x}\text{La}_x\text{B}_6$ is also studied. It is pointed out that there is a unique feature in the NMR spectra, if the $\Gamma_5(T_x^\beta = T_y^\beta = T_z^\beta)$ AFO ordering is realized in $\text{Ce}_{1-x}\text{La}_x\text{B}_6$. Namely, the hyperfine splitting of a B atom pair on the $(\frac{1}{2}, \frac{1}{2}, \pm u)$ sites crosses zero on the $(1\bar{1}0)$ plane when the magnetic field is rotated around the $[001]$ axis.

KEYWORDS: antiferro-octupolar order, octupolar moment, hyperfine interaction, NMR, NpO_2 , CeB_6 , antiferro-quadrupolar order

1. Introduction

The antiferro-octupolar (AFO) moments, which are odd in time-reversal symmetry but are distinct from dipole moments, are now widely recognized as a “hidden” order parameter.¹ The AFO order is a promising candidate to resolve the breaking of the time reversal symmetry without the antiferromagnetic dipole (AFM) order. However, a direct observations of the AFO is very difficult.

There are two ways to realize the AFO moments. One is induced AFO moments in the antiferro-quadrupolar (AFQ) state by applying the static magnetic field.² Another is a spontaneous AFO ordering, which has been recently proposed for NpO_2 and $\text{Ce}_{1-x}\text{La}_x\text{B}_6$.³⁻⁸ In

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this paper, we wish to study a possibility to detect the AFO moments in NMR experiments through the hyperfine interaction. For this purpose we derive a general form of the hyperfine interaction between the multipolar moments and the nuclear spin. Actually we studied this problem before for CeB_6 . The approach was to derive a phenomenological form of the hyperfine interaction from the symmetry.^{9,10} However, there is a simpler and equivalent approach, which we use in this work. It is a straightforward generalization of ref.11, in which the invariant coupling form between multipolar moments was derived by using a method of symmetrized molecular orbital theory. The usefulness of this approach to discuss the hyperfine interaction will be demonstrated in this paper.

To have octupolar moments as independent local degrees of freedom, the material must have high symmetry such as cubic. There are three cubic systems for which the AFO order of some sort is either realized or is likely to be realized. The first system is CeB_6 , which has been studied extensively.^{10,12-14} There are a number of anomalous features in the phase diagram as well as in the nature of the low-temperature order phases, phase II in particular. They are naturally explained by noting the interaction effect between the *field-induced AFO moments*, especially of the T_{xyz} type (Γ_2 type).^{10,15} However, a crucial progress was achieved, when the apparent inconsistency between the neutron diffraction¹⁶ and NMR¹⁷ for the phase II was successfully resolved by recognizing that the hyperfine coupling is present between the B nuclear spin and the induced T_{xyz} AFO moment of Ce ion.^{9,10,18} This is the first case in which the contribution from AFO moments to the hyperfine coupling has been discovered. Therefore the NMR is now regarded as a direct proof for the field-induced AFO moment in CeB_6 .

The second system is NpO_2 ; the nature of the order in NpO_2 below 26K was a mystery for a long time. Carrying out a resonant X-ray scattering, Paixão *et. al.* have recently suggested that their results can be explained well by assuming the triple \mathbf{q} AFQ order of Γ_5 type.⁴ They proposed the triple \mathbf{q} AFO as the primary order parameter because any dipole order have not been observed though Np^{4+} is the Kramers ion. The triple \mathbf{q} AFQ is induced from the primary triple \mathbf{q} AFO. A new development on this problem has been brought by Tokunaga *et. al.*'s ^{17}O ($I = 5/2$) NMR experiment for polycrystalline samples.¹⁹ They found that the O ion sites, which are equivalent in the high temperature phase ($Fm\bar{3}m$), split into two inequivalent groups. The experimental results have the following unique features:

- (I) 1/4 of the ^{17}O nuclei contributes to a sharp resonance line, while the rest 3/4 gives a broad resonance line.
- (II) The shift of the sharp line is approximately proportional to the strength of the applied magnetic field.
- (III) The width of the broad line is given as the sum of a constant and a part proportional to the strength of the magnetic field.

(IV) The shift of the sharp line and the magnetic field induced width of the broad line have comparable magnitude.

We show in this paper that those experimental results can be naturally explained by the quadrupolar field and the hyperfine field splitting in the triple \mathbf{q} state. The hyperfine field is caused by the AFO and/or AFM moment induced by the application of the magnetic field. Therefore the ^{17}O NMR is a fingerprint of the triple \mathbf{q} order of AFO and AFQ.

The third system is $\text{Ce}_x\text{La}_{1-x}\text{B}_6$. It is known that different from pure CeB_6 a new phase, which is called phase IV, appears instead of phase II in the low magnetic field region of $\text{Ce}_x\text{La}_{1-x}\text{B}_6$ ($x \sim 0.75$).^{20–22} The nature of phase IV remains controversial. The time reversal symmetry breaking is reported for this phase.^{23,24} However, no indication of the AFM order has been detected experimentally, although neutron diffraction studies were carried out extensively.²⁵ A characteristic cusp of the magnetic susceptibility has been observed at the transition temperature between phase I and phase IV.⁸ From these results together with other experimental indications,^{20–22,26,27} an AFO order of the Γ_5 type has been recently proposed for the phase IV.^{6–8} A recent NMR experiment indicated a broadening of NMR lines in the phase IV, showing a sign of time reversal symmetry breaking.²³ No further information is obtained from this NMR experiment. Quite recently, the importance of the uniaxial stress to remove the ambiguities due to the domain structure has been demonstrated. Morie *et. al.* pointed out that the magnetic susceptibility shows an anisotropy in contrast to the isotropic behaviors reported previously for ambient pressure.²⁸ This result is qualitatively similar to what one obtains theoretically from the AFO of the Γ_5 type with $\langle T_x^\beta \rangle = \langle T_y^\beta \rangle = \langle T_z^\beta \rangle$. Here, T_x^β , T_y^β and T_z^β are the three components of the Γ_5 type octupolar moment.²⁹ The NMR study under uniaxial stress is desirable to clarify the situation for phase IV. In this paper we will point out a possibility to identify the T^β type AFO order through the NMR experiment. We will show that if the $\langle T_x^\beta \rangle = \langle T_y^\beta \rangle = \langle T_z^\beta \rangle$ type order is realized as Kubo and Kuramoto, and Morie *et. al.* assumed,^{6,28} a characteristic feature of the NMR splitting should be present in the field-direction dependence of the B NMR from $(\frac{1}{2}, \frac{1}{2}, \pm u)$ sites.

This paper is organized as follows. In §2, the hyperfine interaction with multipolar moments of 4f electrons is derived for NpO_2 on the basis of new method. In §3, the recent ^{17}O NMR experiment on NpO_2 is studied theoretically to show that it is consistent with the triple \mathbf{q} structure of AFO and AFQ. In §4, the hyperfine interaction in CeB_6 is re-derived. The field direction dependence of the NMR line is discussed in §5, having the phase IV problem in our mind.

2. Invariant Coupling in NpO_2 and Splitting of O sites into Non-equivalent Sites

The Np ions in NpO_2 form the f.c.c. lattice. The position vector $\boldsymbol{\rho}$ of the eight O ions in the f.c.c. cube is given in Table II, where the length of the edge of the cube is chosen as $2a$. The local symmetry around the O sites has the T_d character. From the discussions described

in Appendix A, the hyperfine interaction of the ^{17}O nuclear spin ($I = 5/2$) located at $\boldsymbol{\rho}$ with multipolar moments of Np 5f electrons is given by

$$\begin{aligned}
H_{\text{hf}}(\boldsymbol{\rho}) = & e^{i\mathbf{q}\cdot\boldsymbol{\rho}} I_x(\boldsymbol{\rho}) \left[c_{1,1} \frac{4}{\sqrt{4}} J_x(\mathbf{q}) (c_x c_y c_z - i \text{sg}(\boldsymbol{\rho}) s_x s_y s_z) \right. \\
& + c_{1,2} \frac{4}{\sqrt{16}} \left\{ J_y(\mathbf{q}) (i \text{sg}(\boldsymbol{\rho}) s_z c_x c_y - c_z s_x s_y) \right. \\
& \quad \left. + J_z(\mathbf{q}) (i \text{sg}(\boldsymbol{\rho}) s_y c_z c_x - c_y s_z s_x) \right\} \\
& + c_{1,3} \frac{4}{\sqrt{8}} \left\{ T_y^\beta(\mathbf{q}) \left\{ i \text{sg}(\boldsymbol{\rho}) s_z c_x c_y - c_z s_x s_y \right\} \right. \\
& \quad \left. - T_z^\beta(\mathbf{q}) (i \text{sg}(\boldsymbol{\rho}) s_y c_z c_x - c_y s_z s_x) \right\} \\
& \left. + c_{1,4} \frac{4}{\sqrt{4}} T_{xyz}(\mathbf{q}) (i \text{sg}(\boldsymbol{\rho}) s_x c_y c_z - c_x s_y s_z) \right] \\
& + (\text{cyclic permutation of } x, y \text{ and } z) .
\end{aligned} \tag{1}$$

Here $c_{i,j}$'s are coupling constants, and $\text{sg}(\boldsymbol{\rho}) = (-1)^{(\rho_x + \rho_y + \rho_z - \frac{a}{2})/a}$, and $c_\nu(s_\nu)$ represents $\cos(q_\nu/2)$ ($\sin(q_\nu/2)$). The summation over \mathbf{q} is assumed in eq. (1). Under the cubic rotation group the octupolar operator of Γ_4 type has the same symmetry character with the dipole operator. Therefore the dipole operator \mathbf{J} in eq. (1) should be read as a linear combination of the pure dipole and the octupolar operator of Γ_4 type. The terms containing the factor $i \text{sg}(\boldsymbol{\rho})$ are due to the T_d site symmetry around each O ion. The imaginary factor in this quantity is only a seeming, which is compensated by the factor $e^{i\mathbf{q}\cdot\boldsymbol{\rho}}$.

Let us assume the Γ_5 AFO order of triple \mathbf{q} type: $T_x^\beta(\mathbf{R}) = T_x^\beta e^{i\mathbf{Q}_x \cdot \mathbf{R}}$, $T_y^\beta(\mathbf{R}) = T_y^\beta e^{i\mathbf{Q}_y \cdot \mathbf{R}}$ and $T_z^\beta(\mathbf{R}) = T_z^\beta e^{i\mathbf{Q}_z \cdot \mathbf{R}}$, with $\mathbf{Q}_x = \pi(1, 0, 0)$, $\mathbf{Q}_y = \pi(0, 1, 0)$ and $\mathbf{Q}_z = \pi(0, 0, 1)$, as assumed in ref. (4). Then we easily find from eq. (1) that the AFO moments in this order do not induce any hyperfine field on the O atoms.

As noted in refs. (4) and (11) and seen from Table I, the triple \mathbf{q} ordering induces the AFQ of the Γ_5 type: $O_{yz}(\mathbf{R}) = O_{yz} e^{i\mathbf{Q}_x \cdot \mathbf{R}}$, $O_{zx}(\mathbf{R}) = O_{zx} e^{i\mathbf{Q}_y \cdot \mathbf{R}}$ and $O_{xy}(\mathbf{R}) = O_{xy} e^{i\mathbf{Q}_z \cdot \mathbf{R}}$. If $O_{yz} = O_{zx} = O_{xy} \equiv O_{\Gamma_5}$ hold, the cubic symmetry of the crystal is not broken.

Let us consider the quadrupolar interaction between the ^{17}O nuclear moment on $\boldsymbol{\rho}$ and the quadrupolar moment of Np ion. The interaction form is given by following the discussion in Appendix B:

$$\begin{aligned}
H_{\text{qq}}(\boldsymbol{\rho}) = & e^{i\mathbf{p}\cdot\mathbf{q}} \left[c_{2,1} \frac{4}{\sqrt{4}} ((O_u(\boldsymbol{\rho}) O_{u,\mathbf{q}} + O_v(\boldsymbol{\rho}) O_{v,\mathbf{q}}) (c_x c_y c_z - i \text{sg}(\boldsymbol{\rho}) s_x s_y s_z)) \right. \\
& + c_{2,2} \frac{8}{\sqrt{24}} \left(\frac{1}{2} (-O_u(\boldsymbol{\rho}) + \sqrt{3} O_v(\boldsymbol{\rho})) O_{yz,\mathbf{q}} (-i \text{sg}(\boldsymbol{\rho}) s_x c_y c_z + c_x s_y s_z) \right. \\
& \quad \left. + O_u(\boldsymbol{\rho}) O_{xy,\mathbf{q}} (-i \text{sg}(\boldsymbol{\rho}) s_z c_x c_y + c_z s_x s_y) \right. \\
& \quad \left. + \frac{1}{2} (-O_u(\boldsymbol{\rho}) - \sqrt{3} O_v(\boldsymbol{\rho})) O_{zx,\mathbf{q}} (-i \text{sg}(\boldsymbol{\rho}) s_y c_z c_x + c_y s_z s_x) \right) \\
& \left. + c_{2,3} \frac{4}{\sqrt{4}} (O_{yz}(\boldsymbol{\rho}) \frac{1}{2} (-O_{u,\mathbf{q}} + \sqrt{3} O_{v,\mathbf{q}}) (i \text{sg}(\boldsymbol{\rho}) s_x c_y c_z - c_x s_y s_z) \right.
\end{aligned}$$

$$\begin{aligned}
& +O_{zx}(\boldsymbol{\rho})\frac{1}{2}(-O_{v,\mathbf{q}} - \sqrt{3}O_{v,\mathbf{q}})(\text{isg}(\boldsymbol{\rho})s_y c_z c_x - c_y s_z s_x) \\
& +O_{xy}(\boldsymbol{\rho})O_{u,\mathbf{q}}(\text{isg}(\boldsymbol{\rho})s_z c_x c_y - c_z s_x s_y)) \\
& + c_{2,4}\frac{4}{\sqrt{4}}((O_{yz}(\boldsymbol{\rho})O_{yz,\mathbf{q}} + O_{zx}(\boldsymbol{\rho})O_{zx,\mathbf{q}} + O_{xy}(\boldsymbol{\rho})O_{xy,\mathbf{q}})(c_x c_y c_z + \text{isg}(\boldsymbol{\rho})s_x s_y s_z)) \\
& + c_{2,5}\frac{4}{\sqrt{8}}(O_{yz}(\boldsymbol{\rho})(O_{zx,\mathbf{q}}(\text{isg}(\boldsymbol{\rho})s_z c_x c_y - c_z s_x s_y) + O_{xy,\mathbf{q}}(\text{isg}(\boldsymbol{\rho})s_y c_z c_x - c_y s_z s_x)) \\
& +(\text{cyclic permutation of } x, y \text{ and } z))\Big]. \tag{2}
\end{aligned}$$

We can derive the quadrupolar interaction between the nuclear quadrupole of ^{17}O and the triple \mathbf{q} AFQ of Np 5f electrons as

$$\begin{aligned}
H_{\text{qq}}(\boldsymbol{\rho}, c_{2,2}) &= C_{2,2}(-\text{isg}(\boldsymbol{\rho}))\left[\frac{1}{2}\left(-O_u(\boldsymbol{\rho}) + \sqrt{3}O_v(\boldsymbol{\rho})\right)O_{yz}e^{i\mathbf{Q}_x\boldsymbol{\rho}}\right. \\
&\quad \left.+O_u(\boldsymbol{\rho})O_{xy}e^{i\mathbf{Q}_z\boldsymbol{\rho}} + \frac{1}{2}\left(-O_u(\boldsymbol{\rho}) - \sqrt{3}O_v(\boldsymbol{\rho})\right)O_{zx}e^{i\mathbf{Q}_y\boldsymbol{\rho}}\right], \tag{3}
\end{aligned}$$

where the quantity $C_{2,2}$ is proportional to $c_{2,2}$ and the order parameter of AFQ O_{Γ_5} , or square of the order parameter of AFO $(T^\beta)^2$, i.e. $C_{2,2} \propto c_{2,2}O_{\Gamma_5} \propto c_{2,2}(T^\beta)^2$. This interaction originates from the coupling caused by the T_d symmetry, such as $s_z c_x c_y$ term in eq.(2). At the $\boldsymbol{\rho}_1 = \frac{1}{2}(3a, 3a, 3a)$ site, the factor $-\text{isg}(\boldsymbol{\rho}_1)e^{i\mathbf{Q}_\nu\boldsymbol{\rho}_1}$ takes 1 for all ν . Therefore it gives the following expression

$$\begin{aligned}
H_{\text{qq}}(\boldsymbol{\rho}_1, c_{2,2}) &= -C_{2,2}\left[O_u(\boldsymbol{\rho}_1)\left(-\frac{1}{2}O_{yz} + O_{xy} - \frac{1}{2}O_{zx}\right)\right. \\
&\quad \left.+\frac{\sqrt{3}}{2}O_v(\boldsymbol{\rho}_1)(O_{yz} - O_{zx})\right]. \tag{4}
\end{aligned}$$

If $O_{yz} = O_{zx} = O_{xy} \equiv O_{\Gamma_5}$ holds, this interaction is canceled out on the $\boldsymbol{\rho}_1$ site.

On the other hand, at the site $\boldsymbol{\rho}_2 = \frac{1}{2}(3a, 3a, a)$, the factor take $-1, -1$ and 1 , respectively, for the terms characterized by the vectors, $\mathbf{Q}_x, \mathbf{Q}_y$ and \mathbf{Q}_z . Then we have

$$\begin{aligned}
H_{\text{qq}}(\boldsymbol{\rho}_2, c_{2,2}) &= C_{2,2}\left[O_u(\boldsymbol{\rho}_2)\left(-\frac{1}{2}O_{yz} - O_{xy} - \frac{1}{2}O_{zx}\right)\right. \\
&\quad \left.+\frac{3}{2}O_v(\boldsymbol{\rho}_2)(O_{yz} - O_{zx})\right], \\
&= C_{2,2}O_u(\boldsymbol{\rho}_2)(-2O_{\Gamma_5}). \tag{5}
\end{aligned}$$

Therefore the quadrupolar field remains on this O atom. A similar calculation can be carried out for other sites and the result is shown in Table III. (The sign of $-\text{isg}(\boldsymbol{\rho})e^{i\mathbf{Q}_\nu\boldsymbol{\rho}}$ is given in the Table II.) We note O_u of the ^{17}O nucleus ($I = 5/2$) is proportional to $3I_z^2 - I(I+1)$, and $-\frac{1}{2}(O_u + \sqrt{3}O_v) \propto 3I_y^2 - I(I+1)$, and $-\frac{1}{2}(O_u - \sqrt{3}O_v) \propto 3I_x^2 - I(I+1)$. The triple \mathbf{q} AFQ order causes 4 different quadrupolar fields on the eight O sites in the fcc cube: a pair of cubic sites (with zero quadrupolar field) and 3 pairs of uniaxial-symmetry sites (each of which has principal axis along one of the x, y and z axes). The ^{17}O nucleus on the non-cubic site will show the quadrupolar splitting of the spectrum. The appearance of the cubic and non-cubic site in the triple \mathbf{q} AFO state can be understood in an intuitive way as explained

Table I. Product of Γ_5 octupolar moment arranged as the quadrupolar moments.

Γ_5	$O_{yz} = T_y^\beta T_z^\beta$	$O_{zx} = T_z^\beta T_x^\beta$	$O_{xy} = T_x^\beta T_y^\beta$
Γ_3	$O_u = \frac{1}{\sqrt{6}}(-T_x^\beta T_x^\beta - T_y^\beta T_y^\beta + 2T_z^\beta T_z^\beta)$ $O_v = \frac{1}{\sqrt{2}}(T_x^\beta T_x^\beta - T_y^\beta T_y^\beta)$		

in Figs. 1 and 2. The colored cubes are the cubic sites and their neighboring three sites have principal axis along the x, y and z axes.

The quadrupolar field of the type O_{yz} , O_{zx} and O_{xy} on O atoms is not induced in the triple \mathbf{q} ordering.

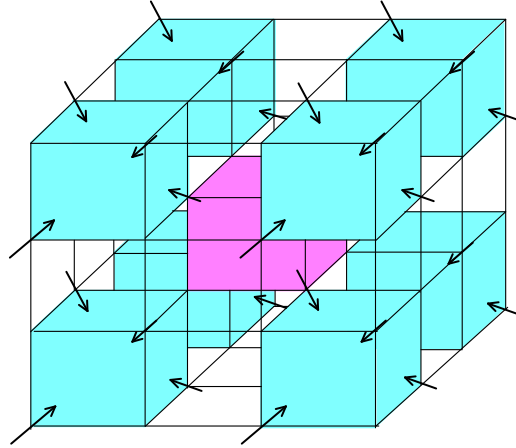


Fig. 1. Schematics for the triple \mathbf{q} ordering of T^β AFO. The T^β moments on Np ions are denoted by arrows. The O sites are located at the centers of colored and colorless cubes. The unit cell of the ordered phase is composed of four Np and eight O sites. See also Fig. 2 for details.

3. Magnetic Field Effect in NpO_2

The applied magnetic field induces AFM moments with the same wave vector. They can be derived by using the Table III of ref. 11:

$$\begin{aligned}
 J_x(\mathbf{R}) &= \frac{b(\Gamma_4, \Gamma_5)}{\sqrt{2}} \left(O_{xy} H_y e^{i\mathbf{Q}_z \cdot \mathbf{R}} + O_{zx} H_z e^{i\mathbf{Q}_y \cdot \mathbf{R}} \right) \\
 &= \frac{b(\Gamma_4, \Gamma_5)}{\sqrt{2}} O_{\Gamma_5} \left(H_y e^{i\mathbf{Q}_z \cdot \mathbf{R}} + H_z e^{i\mathbf{Q}_y \cdot \mathbf{R}} \right), \tag{6}
 \end{aligned}$$

$$J_y(\mathbf{R}) = \frac{b(\Gamma_4, \Gamma_5)}{\sqrt{2}} O_{\Gamma_5} \left(H_x e^{i\mathbf{Q}_z \cdot \mathbf{R}} + H_z e^{i\mathbf{Q}_x \cdot \mathbf{R}} \right), \tag{7}$$

$$J_z(\mathbf{R}) = \frac{b(\Gamma_4, \Gamma_5)}{\sqrt{2}} O_{\Gamma_5} \left(H_x e^{i\mathbf{Q}_y \cdot \mathbf{R}} + H_y e^{i\mathbf{Q}_x \cdot \mathbf{R}} \right), \tag{8}$$

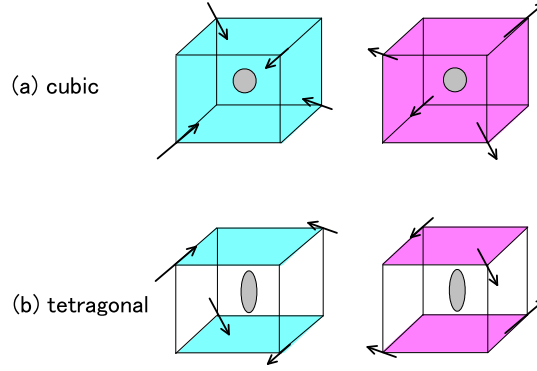


Fig. 2. Environments around O sites located at the center of cubes. There are eight nonequivalent O sites. (a) Two of them are subject to cubic fields. Four arrows point the center of the blue cube, whereas they go out from the center of the red cube. Both keep four trigonal axes, so that a cubic symmetry is retained there. (b) Two O sites in the colorless cubes are neighboring with blue and red colored cubes along z axis. Thus, the trigonal symmetry is broken there, and they are subject to tetragonal fields. There are other four O sites neighboring with colored cubes along x and y axes, respectively. These can be represented by the corresponding rotations of the figure (b).

Table II. The sign of $-isg(\rho)e^{i\mathbf{Q} \cdot \rho}$ on eight O sites and the hyperfine field on O sites. The column of $\mathbf{Q} \cdot \rho$ shows $-isg(\rho)e^{i\mathbf{Q} \cdot \rho}$. The last column shows H_{hf} , eq.(9) except for the factor $C_{1,2}$.

site(ρ)	\mathbf{Q}_x	\mathbf{Q}_y	\mathbf{Q}_z	total
$\frac{a}{2}(3, 3, 3)$	1	1	1	$2\mathbf{I} \cdot \mathbf{H}$
$\frac{a}{2}(3, 3, 1)$	-1	-1	1	$-2I_z H_z$
$\frac{a}{2}(1, 1, 3)$	-1	-1	1	$-2I_z H_z$
$\frac{a}{2}(1, 1, 1)$	1	1	1	$2\mathbf{I} \cdot \mathbf{H}$
$\frac{a}{2}(3, 1, 3)$	-1	1	-1	$-2I_y H_y$
$\frac{a}{2}(3, 1, 1)$	1	-1	-1	$-2I_x H_x$
$\frac{a}{2}(1, 3, 3)$	1	-1	-1	$-2I_x H_x$
$\frac{a}{2}(1, 3, 1)$	-1	1	-1	$-2I_y H_y$

where $b(\Gamma_4, \Gamma_5)$ is a proportionality constant. Substituting this expression into eq. (1), we obtain the hyperfine field as

$$\begin{aligned}
 H_{\text{hf}}(\rho, c_{1,2}) = & C_{1,2}isg(\rho) \left[I_x H_x \left(e^{i\mathbf{Q}_y \cdot \rho} + e^{i\mathbf{Q}_z \cdot \rho} \right) \right. \\
 & \left. + I_y H_y \left(e^{i\mathbf{Q}_z \cdot \rho} + e^{i\mathbf{Q}_x \cdot \rho} \right) + I_z H_z \left(e^{i\mathbf{Q}_x \cdot \rho} + e^{i\mathbf{Q}_y \cdot \rho} \right) \right], \quad (9)
 \end{aligned}$$

Table III. Quadrupolar field on eight O sites. O_u and O_v are the quadrupolar operators of O nucleus.The last column shows the result for $O_{yz} = O_{zx} = O_{xy} \equiv O_{\Gamma_5}$

site(ρ)	O_u	O_v	total
$\frac{a}{2}(3, 3, 3)$	$\frac{1}{2}O_{yz} - O_{xy} + \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(-O_{yz} + O_{zx})$	0
$\frac{a}{2}(3, 3, 1)$	$-\frac{1}{2}O_{yz} - O_{xy} - \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(O_{yz} - O_{zx})$	$-2O_u O_{\Gamma_5}$
$\frac{a}{2}(1, 1, 3)$	$-\frac{1}{2}O_{yz} - O_{xy} - \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(O_{yz} - O_{zx})$	$-2O_u O_{\Gamma_5}$
$\frac{a}{2}(1, 1, 1)$	$\frac{1}{2}O_{yz} - O_{xy} + \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(-O_{yz} + O_{zx})$	0
$\frac{a}{2}(3, 1, 3)$	$-\frac{1}{2}O_{yz} + O_{xy} + \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(O_{yz} + O_{zx})$	$(O_u + \sqrt{3}O_v)O_{\Gamma_5}$
$\frac{a}{2}(3, 1, 1)$	$\frac{1}{2}O_{yz} + O_{xy} - \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(-O_{yz} - O_{zx})$	$(O_u - \sqrt{3}O_v)O_{\Gamma_5}$
$\frac{a}{2}(1, 3, 3)$	$\frac{1}{2}O_{yz} + O_{xy} - \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(-O_{yz} - O_{zx})$	$(O_u - \sqrt{3}O_v)O_{\Gamma_5}$
$\frac{a}{2}(1, 3, 1)$	$-\frac{1}{2}O_{yz} + O_{xy} + \frac{1}{2}O_{zx}$	$\frac{\sqrt{3}}{2}(-O_{yz} - O_{zx})$	$(O_u + \sqrt{3}O_v)O_{\Gamma_5}$

where the quantity $C_{1,2}$ is proportional to $c_{1,2}$ and the AFQ order parameter, i.e. $C_{1,2} \propto c_{1,2}O_{\Gamma_5}b(\Gamma_4, \Gamma_5)$. This type of interaction appears through the coupling term with the constant $c_{1,2}$ in eq. (1). If one considers only the term of the type $\vec{I} \cdot \vec{J}$, which has the coupling constant $c_{1,1}$ in eq. (1), the interaction expressed by eq. (9) will not appear. In addition, this interaction originates from the coupling caused by the T_d symmetry, such as $s_z c_x c_y$ term in eq.(1).

At the $\rho_1 = \frac{1}{2}(3a, 3a, 3a)$ site, the factor $-isg(\rho_1)e^{i\mathbf{Q} \cdot \rho_1}$ takes 1 for all ν . Therefore we have $H_{\text{hf}}(\rho_1, c_{1,2}) = -2C_{1,2}\vec{I} \cdot \vec{H}$. On the other hand, at the site $\rho_2 = \frac{1}{2}(3a, 3a, a)$, the factor takes $-1, -1$ and 1 , respectively, for the terms having $\mathbf{Q}_x, \mathbf{Q}_y$ and \mathbf{Q}_z . Then we have $H_{\text{hf}}(\rho_2, c_{1,2}) = 2C_{1,2}I_z H_z$. Clearly the hyperfine field on the ρ_1 site is different from that on the ρ_2 site. We find in this way that the eight O sites split into four inequivalent sites also in hyperfine interaction, as summarized in Table II. When the magnetic field is given by (H_x, H_y, H_z) , four types of the hyperfine field are induced on the O atoms: $2C_{1,2}(H_x, H_y, H_z)$, $2C_{1,2}(0, 0, -H_z)$, $2C_{1,2}(0, -H_y, 0)$, and $2C_{1,2}(-H_x, 0, 0)$.

For polycrystalline samples we have to take an average of the splitting over the direction. Then, we find that the first group does not show any broadening of the resonance, because the hyperfine field is always induced in the direction of the applied field. On the other hand, the hyperfine field usually deviates from the direction of the field in the other three groups. This will cause the broadening of the resonance spectrum with the line shape of the powder pattern of the axial symmetry crystal.

Let us remember that the magnetic field usually induces the AFO moments of the types, T^β (whose wave number vector is not equal to that of the original one) and T_{xyz} , as shown in Table III of ref. 11. The hyperfine field on the O atoms is induced also through these moments

as can be seen in eq. (1). They give the hyperfine field of the type:

$$H_{\text{hf}}(\boldsymbol{\rho}, c_{1,3}) = -C_{1,3} \text{isg}(\boldsymbol{\rho}) \left[I_x H_x \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) + I_y H_y \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) + I_z H_z \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) \right], \quad (10)$$

$$H_{\text{hf}}(\boldsymbol{\rho}, c_{1,4}) = C_{1,4} \text{isg}(\boldsymbol{\rho}) \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} I_x H_x + e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} I_y H_y + e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} I_z H_z \right), \quad (11)$$

where $C_{1,3} \propto c_{1,3} O_{\Gamma_5}$ and $C_{1,4} \propto c_{1,4} O_{\Gamma_5}$. The former gives the hyperfine field $-2C_{1,3}(0, 0, 0)$, $-2C_{1,3}(H_x, H_y, 0)$, $-2C_{1,3}(0, H_y, H_z)$, and $-2C_{1,3}(H_x, 0, H_z)$, whereas the latter gives $C_{1,4}(H_x, H_y, H_z)$, $C_{1,4}(-H_x, -H_y, H_z)$, $C_{1,4}(H_x, -H_y, -H_z)$, and $C_{1,4}(-H_x, H_y, -H_z)$.

To apply this theory to NpO_2 , we have to sum up these three contributions. Even after the summation we still have a sharp line and a broad line; the shift of the sharp line and the field induced part of the width of the broad line have comparable magnitude; they are proportional to the strength of the magnetic field in low field region.

Our theory has already predicted that the quadrupolar splitting with uniaxial symmetry appears on the non-cubic O site in the ordered phase of NpO_2 . Even at zero field, this quadrupolar splitting exists. By the application of the magnetic field in the AFO state, the AFQ is also induced as given in the table IV. We can see that the induced quadrupolar moments of the Γ_5 type: $O_{yz}(\mathbf{R}) = \frac{c(\Gamma_5, \Gamma_5)}{\sqrt{2}} (H_z T_y^\beta e^{i\mathbf{Q} \cdot \mathbf{R}} - H_y T_z^\beta e^{i\mathbf{Q} \cdot \mathbf{R}})$, $O_{zx}(\mathbf{R}) = \frac{c(\Gamma_5, \Gamma_5)}{\sqrt{2}} (H_x T_z^\beta e^{i\mathbf{Q} \cdot \mathbf{R}} - H_z T_x^\beta e^{i\mathbf{Q} \cdot \mathbf{R}})$ and $O_{xy}(\mathbf{R}) = \frac{c(\Gamma_5, \Gamma_5)}{\sqrt{2}} (H_y T_x^\beta e^{i\mathbf{Q} \cdot \mathbf{R}} - H_x T_y^\beta e^{i\mathbf{Q} \cdot \mathbf{R}})$ cause the quadrupolar splitting. Here $c(\Gamma_5, \Gamma_5)$ is the proportionality coefficient in Table IV. Substituting these results into eq. (2), we obtain,

$$H_{\text{qf}}(\boldsymbol{\rho}, c_{2,5}) = C_{2,5} \text{isg}(\boldsymbol{\rho}) \left[O_{yz}(\boldsymbol{\rho}) H_x \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) + O_{zx}(\boldsymbol{\rho}) H_y \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) + O_{xy}(\boldsymbol{\rho}) H_z \left(e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} - e^{i\mathbf{Q} \cdot \boldsymbol{\rho}} \right) \right] \quad (12)$$

where $C_{2,5} \propto c_{2,5} c(\Gamma_5, \Gamma_5) T^\beta$. The phase factor of this expression has the same form as that of eq. (10); thus it will be canceled out on the cubic sites. On the non-cubic sites, the quadrupolar interaction terms of the type $C_{2,5}[O_{yz}H_x + O_{zx}H_y]$, $C_{2,5}[O_{zx}H_y + O_{xy}H_z]$ and $C_{2,5}[O_{xy}H_z + O_{yz}H_x]$ are expected.

The broadening due to the quadrupolar splitting is caused at non-cubic sites when the average is taken over the direction for polycrystalline samples. Even at zero field, the broadening due to the quadrupolar splitting will exist.³⁰ Thus, in the low magnetic field region, the broadening of the spectrum originating from the non-cubic site will be the sum of a constant term and the term proportional to a strength of the magnetic field.

The field-induced AFO/AFM moments are proportional to both the magnetic field and the AFQ moment. Therefore they are proportional to the square of the primary AFO moment. Another type of broadening due to the field induced hyperfine splitting is also expected. The AFM and the AFO moments, which are directly proportional to the primary AFO moment and the square of the magnetic field can be also induced. For example, from the $\Gamma_5 - 2$ column

Table IV. Quadrupole moment as a product of magnetic field and octupolar moment.

Quadrupole moment	Γ_5	Γ_2
O_{yz}	$\frac{1}{\sqrt{2}}(-H_y T_z^\beta + H_z T_y^\beta)$	$H_x T_{xyz}$
O_{zx}	$\frac{1}{\sqrt{2}}(-H_z T_x^\beta + H_x T_z^\beta)$	$H_y T_{xyz}$
O_{xy}	$\frac{1}{\sqrt{2}}(-H_x T_y^\beta + H_y T_x^\beta)$	$H_z T_{xyz}$
O_u	$\frac{1}{\sqrt{2}}(-H_x T_x^\beta + H_y T_y^\beta)$	
O_v	$\frac{1}{\sqrt{6}}(-H_x T_x^\beta - H_y T_y^\beta + 2H_z T_z^\beta)$	

Table V. Γ_4 type moment as a product of magnetic field and octupolar moment.

Γ_4 moment	$\Gamma_5 - 1$	$\Gamma_5 - 2$	Γ_2
T_x^α	$-\frac{1}{\sqrt{2}}(H_y^2 - H_z^2)T_x^\beta$	$H_x(H_y T_y^\beta - H_z T_z^\beta)$	$\sqrt{2}H_y H_z T_{xyz}$
T_y^α	$-\frac{1}{\sqrt{2}}(H_z^2 - H_x^2)T_y^\beta$	$H_y(H_z T_z^\beta - H_x T_x^\beta)$	$\sqrt{2}H_z H_x T_{xyz}$
T_z^α	$-\frac{1}{\sqrt{2}}(H_x^2 - H_y^2)T_z^\beta$	$H_z(H_x T_x^\beta - H_y T_y^\beta)$	$\sqrt{2}H_x H_y T_{xyz}$

of Table V and eq. (1), we have the interaction

$$\begin{aligned}
H_{\text{hf}}(\boldsymbol{\rho}) = & C_{1,2} \text{isg}(\boldsymbol{\rho}) \left[I_x H_y H_z \left(e^{i\mathbf{Q}_y \cdot \boldsymbol{\rho}} + e^{i\mathbf{Q}_z \cdot \boldsymbol{\rho}} \right) \right. \\
& \left. + I_y H_z H_x \left(e^{i\mathbf{Q}_z \cdot \boldsymbol{\rho}} + e^{i\mathbf{Q}_x \cdot \boldsymbol{\rho}} \right) + I_z H_x H_y \left(e^{i\mathbf{Q}_x \cdot \boldsymbol{\rho}} + e^{i\mathbf{Q}_y \cdot \boldsymbol{\rho}} \right) \right], \quad (13)
\end{aligned}$$

where $C_{1,2} \propto c_{1,2} T^\beta$. This term has the largest contribution to the cubic site, and the splitting due to this term depends on the field direction as $H^2 h_x h_y h_z$. After averaging over the direction, this effect causes a broadening of spectrum of $O(H^2)$. However, it still gives two contributions with the intensity ratio 1: 3. The equations (9) ~ (11) must contain the $O(H^2)$ terms coming from the change of the order parameters.

Finally we conclude that the shift of the sharp line, ω_s depend on the field strength as $\omega_s = a_s^{(s)} H + O(H^2)$. The width of the sharp line, Δ_s will be given as a higher order function of H , i.e. $\Delta_s = O(H^2)$. The width of the broad line, Δ_b , is given as $\Delta_b = c_b^{(w)} + a_b^{(w)} H + O(H^2)$, while the shift of the broad line, ω_b is $\omega_b = a_b^{(s)} H + O(H^2)$. The constant $c_b^{(w)}$ is caused by the quadrupolar splitting. If the hyperfine interaction is the main mechanism, the constants $a_s^{(s)}$, $a_b^{(w)}$, $a_b^{(s)}$ will have same order of magnitude. $a_b^{(s)}$ and $a_b^{(w)}$ are related to the angle average of the axial symmetric sites. These four constants are proportional to the AFQ moment; thus they must have almost the same temperature dependence. If the magnetic field induced AFQ in the AFO state, eq (12), has appreciable contribution, its effect will appear mainly in the $a_b^{(w)}$ term. This contribution is directly proportional to the AFO order parameter.

Table VI. Γ_5 type moment as a product of magnetic field and octupolar moment.

Γ_5 moment	$\Gamma_5 - 1$	$\Gamma_5 - 2$	$\Gamma_5 - 3$
T_x^β	$-\frac{1}{\sqrt{6}}(2H_x^2 - H_y^2 - H_z^2)T_x^\beta$	$-H_x(H_yT_y^\beta + H_zT_z^\beta)$	$\frac{1}{\sqrt{3}}H^2T_x^\beta$
T_y^β	$-\frac{1}{\sqrt{6}}(2H_y^2 - H_x^2 - H_z^2)T_y^\beta$	$-H_y(H_zT_z^\beta + H_xT_x^\beta)$	$\frac{1}{\sqrt{3}}H^2T_y^\beta$
T_z^β	$-\frac{1}{\sqrt{6}}(2H_z^2 - H_x^2 - H_y^2)T_z^\beta$	$-H_z(H_xT_x^\beta + H_yT_y^\beta)$	$\frac{1}{\sqrt{3}}H^2T_z^\beta$

4. Hyperfine Interaction with Multipolar Moments in CeB_6 and $\text{Ce}_x\text{La}_{1-x}\text{B}_6$

CeB_6 has the crystal structure of CaB_6 type. The Ce ions form the s.c. lattice. Let us denote the B ion site $(\frac{a}{2}, \frac{a}{2}, \pm ua)$ as $\boldsymbol{\rho}_{z,\pm} = (0, 0, \pm\frac{1}{2})$, where u is a parameter for the position of B atom and a is the lattice constant of the s.c. lattice. If we follow the method described in Appendix C, the interaction of the nuclear spin \mathbf{I} of B atom with the multipolar moments of Ce ions is given by

$$\begin{aligned}
H_{\text{hf}}(\boldsymbol{\rho}_{z,\pm}) = & \frac{4}{\sqrt{4}} e^{i\frac{qx+qy+qz}{2}} a e^{i\mathbf{q} \cdot \boldsymbol{\rho}_{z,\pm}} \left[I_z(\boldsymbol{\rho}_{z,\pm}) \left\{ c_{1,1} J_z(\mathbf{q}) c_x c_y \right. \right. \\
& + \text{isg}(\boldsymbol{\rho}_{z,\pm}) \frac{c_{1,2}}{\sqrt{2}} \left(J_x(\mathbf{q}) s_x c_y + J_y(\mathbf{q}) c_x s_y \right) + \text{isg}(\boldsymbol{\rho}_{z,\pm}) \frac{c_{1,3}}{\sqrt{2}} \left(T_x^\beta(\mathbf{q}) s_x c_y - T_y^\beta(\mathbf{q}) c_x s_y \right) \\
& \left. \left. - c_{1,4} T_{xyz}(\mathbf{q}) s_x s_y \right\} \right. \\
& + I_x(\boldsymbol{\rho}_{z,\pm}) \left\{ c_{2,1} J_x(\mathbf{q}) c_x c_y + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,2} J_z(\mathbf{q}) s_x c_y - c_{2,3} J_y(\mathbf{q}) s_x s_y \right. \\
& \left. + c_{2,4} T_x^\beta(\mathbf{q}) c_x c_y + c_{2,5} T_y^\beta(\mathbf{q}) s_x s_y + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,6} T_z^\beta(\mathbf{q}) s_x c_y + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,7} T_{xyz}(\mathbf{q}) c_x s_y \right\} \\
& + I_y(\boldsymbol{\rho}_{z,\pm}) \left\{ c_{2,1} J_y(\mathbf{q}) c_x c_y + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,2} J_z(\mathbf{q}) s_y c_x - c_{2,3} J_x(\mathbf{q}) s_x s_y \right. \\
& \left. + c_{2,4} T_y^\beta(\mathbf{q}) c_x c_y - c_{2,5} T_x^\beta(\mathbf{q}) s_x s_y + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,6} T_z^\beta(\mathbf{q}) s_y c_x \right. \\
& \left. \left. + \text{isg}(\boldsymbol{\rho}_{z,\pm}) c_{2,7} T_{xyz}(\mathbf{q}) c_y s_x \right\} \right]. \tag{14}
\end{aligned}$$

Here $c_{i,j}$'s are coupling constants, and $\text{sg}(\boldsymbol{\rho}_{z,\pm}) = \pm 1$. The quantity $c_\nu(s_\nu)$ represents $\cos(q_\nu/2)$ ($\sin(q_\nu/2)$). The result (14) agrees with the result given in ref. 9.

The hyperfine interaction of the B nuclei at the $(\pm ua, \frac{a}{2}, \frac{a}{2})$ site, which is denoted henceforth as $\boldsymbol{\rho}_{x,\pm} = (\pm\frac{1}{2}, 0, 0)$, is obtained by 90° degree rotation around the y -axis: $(I_x, I_y, I_z) \rightarrow (-I_z, I_y, I_x)$, $(T_x^\beta, -T_y^\beta, T_z^\beta) \rightarrow (T_z^\beta, -T_y^\beta, -T_x^\beta)$, $T_{xyz} \rightarrow -T_{xyz}$. At the same time the wave vector is changed as $(q_x, q_y, q_z) \rightarrow (-q_z, q_y, q_x)$ except for the factor in the function $e^{i\frac{qx+qy+qz}{2}} e^{i\mathbf{q} \cdot \boldsymbol{\rho}_{x,\pm}}$. The dipole operator (J_x, J_y, J_z) follows the same transformation to that of the operator (I_x, I_y, I_z) . Similarly, the hyperfine interaction for the B on the $(\frac{a}{2}, \pm ua, \frac{a}{2})$ site, which is denoted as $\boldsymbol{\rho}_{y,\pm} = (0, \pm\frac{1}{2}, 0)$, is obtained by a rotation around the x -axis: $(I_x, I_y, I_z) \rightarrow (I_x, -I_z, I_y)$, $(T_x^\beta, -T_y^\beta, T_z^\beta) \rightarrow (-T_x^\beta, T_z^\beta, -T_y^\beta)$, $T_{xyz} \rightarrow -T_{xyz}$, and $(q_x, q_y, q_z) \rightarrow (q_x, -q_z, q_y)$.

If we assume the $\mathbf{Q} = \pi(1, 1, 1)$ order as done in refs. (7) and (28), the quantities s_ν and c_ν

are reduced to $s_x = s_y = s_z = 1$, and $c_x = c_y = c_z = 0$. Then the hyperfine field is expressed as follows:

$$\begin{aligned}
 H_{\text{hf}}(\boldsymbol{\rho}_{z,\pm}) = & \pm \left[I_z(\boldsymbol{\rho}_{z,\pm})(-C_{1,4}T_{xyz}(\mathbf{Q})) \right. \\
 & + I_x(\boldsymbol{\rho}_{z,\pm}) \left(-C_{2,3}J_y(\mathbf{Q}) + C_{2,5}T_y^\beta(\mathbf{Q}) \right) \\
 & + I_y(\boldsymbol{\rho}_{z,\pm}) \left(-C_{2,3}J_x(\mathbf{Q}) - C_{2,5}T_x^\beta(\mathbf{Q}) \right) \\
 & + I_z(\boldsymbol{\rho}_{z,\pm})(-C_{1,1}J_z(0)) \\
 & \left. + I_x(\boldsymbol{\rho}_{z,\pm}) \left(C_{2,1}J_x(0) + C_{2,4}T_x^\beta(0) \right) + I_y(\boldsymbol{\rho}_{z,\pm}) \left(C_{2,1}J_y(0) + C_{2,4}T_y^\beta(0) \right) \right] \quad (15)
 \end{aligned}$$

Here $T_\nu^\beta(\mathbf{Q})$, $J_\nu(\mathbf{Q})$ and $T_{xyz}(\mathbf{Q})$ are the thermal average of the ordering parameters with wave vector \mathbf{Q} . The quantities for $\mathbf{Q} = 0$ are the uniform components. The factor $C_{i,j}$ is a constant proportional to $c_{i,j}$. Even in the uniform term we have the hyperfine interaction due to the octupolar moment $T_\nu^\beta(0)$. Such term will be induced by the application of the magnetic field under the existence of the uniform component of quadrupolar moment. It is given by a different combination of the quadrupolar moment and the magnetic field from that of $J_{\nu,0}$ term.¹¹ Hereafter we neglect the $\mathbf{Q} = 0$ terms. The hyperfine interaction for $\boldsymbol{\rho}_{x,\pm}$ and $\boldsymbol{\rho}_{y,\pm}$ site is given ,

$$\begin{aligned}
 H_{\text{hf}}(\boldsymbol{\rho}_{x,\pm}) = & \pm \left[I_x(\boldsymbol{\rho}_{x,\pm})(-C_{1,4}T_{xyz}(\mathbf{Q})) \right. \\
 & + I_z(\boldsymbol{\rho}_{x,\pm}) \left\{ -C_{2,3}J_y(\mathbf{Q}) - C_{2,5}T_y^\beta(\mathbf{Q}) \right\} \\
 & \left. + I_y(\boldsymbol{\rho}_{x,\pm}) \left\{ -C_{2,3}J_z(\mathbf{Q}) + C_{2,5}T_z^\beta(\mathbf{Q}) \right\} \right], \quad (16)
 \end{aligned}$$

$$\begin{aligned}
 H_{\text{hf}}(\boldsymbol{\rho}_{y,\pm}) = & \pm \left[I_y(\boldsymbol{\rho}_{y,\pm})(-C_{1,4}T_{xyz}(\mathbf{Q})) \right. \\
 & + I_x(\boldsymbol{\rho}_{y,\pm}) \left\{ -C_{2,3}J_z(\mathbf{Q}) - C_{2,5}T_z^\beta(\mathbf{Q}) \right\} \\
 & \left. + I_z(\boldsymbol{\rho}_{y,\pm}) \left\{ -C_{2,3}J_x(\mathbf{Q}) + C_{2,5}T_x^\beta(\mathbf{Q}) \right\} \right]. \quad (17)
 \end{aligned}$$

If the ordering wave vector \mathbf{q} satisfies $\cos(q_y/2) \neq \cos(q_z/2)$, a mixing of $J_x(\mathbf{q})$ with $T_x^\beta(\mathbf{q})$ through the nearest site interaction on the s.c. lattice^{11,31} will be caused. In addition, the ordering with $\sin(q_\nu) \neq 0$ causes mixing of dipole and T^β type moment through the next nearest site interaction.¹¹ The ordering of the wave vector with $\mathbf{Q} = \pi(1,1,1)$ seems to be a plausible candidate when one considers the pure spontaneous AFO. The n.n. interaction of Γ_5 moment will have comparable magnitude to that of the quadrupolar and magnetic interaction.³¹

5. Dependence of Hyperfine Splitting on the Field Direction in $\text{Ce}_{1-x}\text{La}_x\text{B}_6$

Let us assume that the ordering with $\mathbf{Q} = \pi(1, 1, 1)$ occurs. Then, the hyperfine field splitting $\Delta(z)$ of B-ion pair at $(\frac{a}{2}, \frac{a}{2}, \pm ua)$ is given as

$$\begin{aligned} \Delta(z) = & -2C_{1,4}h_zT_{xyz}(\mathbf{Q}) + 2C_{2,5}(h_xT_y^\beta(\mathbf{Q}) - h_yT_x^\beta(\mathbf{Q})) \\ & -2C_{2,3}(h_xJ_y(\mathbf{Q}) + h_yJ_x(\mathbf{Q})), \end{aligned} \quad (18)$$

where (h_x, h_y, h_z) denotes the direction of the magnetic field. Henceforth we consider the ordering of three types:

- (i) $T_x^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q}) = T_z^\beta(\mathbf{Q}) \equiv \frac{1}{\sqrt{3}}T_{111}^\beta$,
- (ii) $T_x^\beta(\mathbf{Q}) = -T_y^\beta(\mathbf{Q}) \equiv \frac{1}{\sqrt{2}}T_{110}^\beta$, $T_z^\beta(\mathbf{Q}) = 0$,
- (iii) $T_x^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q}) \equiv -\frac{1}{\sqrt{6}}T_{110}^\beta$, and $T_z^\beta(\mathbf{Q}) \equiv \frac{2}{\sqrt{6}}T_{112}^\beta$.

In the case of $T_x^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q})$ ((i) and (iii)), the expression (18) depends on the direction of the magnetic field as $\sin\theta\sin(\phi - \frac{\pi}{4})$. Here the direction of the magnetic field is expressed as $(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. $\Delta(z)$ vanishes at $\phi = \pi/4$, and has linear dependence, as $\Delta(z) \propto \phi - \frac{\pi}{4}$, in the vicinity of $\phi = \frac{\pi}{4}$. In the case of $T_x^\beta(\mathbf{Q}) = -T_y^\beta(\mathbf{Q})$ (case (ii)), $\Delta(z)$ depends on the direction as $\sin\theta\sin(\phi + \frac{\pi}{4})$, showing the maximum at $\phi = \pi/4$.

When the magnetic field is applied, the order parameters are modified. The lowest-order effect is given by the product of the square of the magnetic field and the linear term of the order parameters, because they are the lowest order expression with non-uniform and time reversal odd in the case of AFO ordering. In Table V, we show the induced Γ_4 AFO moment as a product of the Γ_5 AFO moment and the magnetic field. This will also be proportional to the dipole moment. Substituting this into the third term of eq. (18), we have

$$\begin{aligned} & h_xJ_y(\mathbf{Q}) + h_yJ_x(\mathbf{Q}) \\ & = (h_x - h_y) \left[\frac{a_1(\Gamma_4, \Gamma_5)}{\sqrt{2}}(h_x^2 + h_xh_y + h_y^2 - h_z^2) - a_2(\Gamma_4, \Gamma_5)h_xh_y \right] H^2T_\parallel^\beta, \end{aligned} \quad (19)$$

where $a_1(\Gamma_4, \Gamma_5)$ and $a_2(\Gamma_4, \Gamma_5)$ are proportionality constants. Here we introduced $T_x^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q}) \equiv T_\parallel^\beta$. The terms proportional to the order parameter $T_z^\beta(\mathbf{Q})$ do not appear even when it exists. Equation (19) is also proportional to $h_x - h_y$, thus the linear dependence on $\phi - \pi/4$ is not changed. The induced moments of Γ_5 type can be derived also by using the Table VI, but the conclusion is unchanged.

For the order of the type $J_x(\mathbf{Q}) = -J_y(\mathbf{Q})$, the same ϕ dependence as that of $T_x^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q})$ is expected as seen from eq. (18). The field dependence is also similar as one can check easily by using the results of Tables VII and VIII. However, complementary measurements of the splitting for pairs on the other axis, and/or detailed calculations of the direction dependence based on the microscopic model will distinguish them. If the $T_{xyz}(\mathbf{Q})$ order is realized, the dependence of $\Delta(z)$ on the field direction is unique. This has been already noted in ref. 9.

Table VII. Γ_4 type moment as a product of magnetic field and dipole moment

Γ_4 moment	$\Gamma_4 - 1$	$\Gamma_4 - 2$	$\Gamma_4 - 3$
T_x^α	$-\frac{1}{\sqrt{6}}(2H_x^2 - H_y^2 - H_z^2)J_x$	$-H_x(H_yJ_y + H_zJ_z)$	$\frac{1}{\sqrt{3}}H^2J_x$
T_y^α	$-\frac{1}{\sqrt{6}}(2H_y^2 - H_z^2 - H_x^2)J_y$	$-H_y(H_zJ_z + H_xJ_x)$	$\frac{1}{\sqrt{3}}H^2J_y$
T_z^α	$-\frac{1}{\sqrt{6}}(2H_z^2 - H_x^2 - H_y^2)J_z$	$-H_z(H_xJ_x + H_yJ_y)$	$\frac{1}{\sqrt{3}}H^2J_z$

Table VIII. Γ_5 type moment as a product of magnetic field and dipole moment.

Γ_5 moment	$\Gamma_4 - 1$	$\Gamma_4 - 2$
T_x^β	$\frac{1}{\sqrt{2}}(H_y^2 - H_z^2)J_x$	$H_x(H_yJ_y - H_zJ_z)$
T_y^β	$\frac{1}{\sqrt{2}}(H_z^2 - H_x^2)J_y$	$H_y(H_zJ_z - H_xJ_x)$
T_z^β	$\frac{1}{\sqrt{2}}(H_x^2 - H_y^2)J_z$	$H_z(H_xJ_x - H_yJ_y)$

Table IX. $\Gamma_2(\Gamma_1)$ type moment as a product of magnetic field and the $\Gamma_4(\Gamma_5)$ moment

Γ_4	Γ_5
$T_{xyz} = -\sqrt{\frac{2}{3}}(H_yH_zJ_x + H_zH_xJ_y + H_xH_yJ_z)$	$A_1 = \sqrt{\frac{2}{3}}(H_yH_zT_x^\beta + H_zH_xT_y^\beta + H_yH_zT_z^\beta)$

The splitting of the NMR of the B ion pair at $(\pm ua, \frac{a}{2}, \frac{a}{2})$, $\Delta(x)$, is given as

$$\begin{aligned} \Delta(x) = & -2C_{1,4}h_xT_z^\beta(\mathbf{Q}) + 2C_{2,5}\left(h_zT_y^\beta(\mathbf{Q}) - h_yT_z^\beta(\mathbf{Q})\right) \\ & -2C_{2,3}\left(h_zJ_y(\mathbf{Q}) + h_yJ_z(\mathbf{Q})\right). \end{aligned} \quad (20)$$

The splitting of the pair at $(\frac{a}{2}, \pm ua, \frac{a}{2})$, $\Delta(y)$, is similarly given by using eq. (17). When the octupolar ordering follows $T_z^\beta(\mathbf{Q}) = T_y^\beta(\mathbf{Q})$ (type (i)), this expression has a node when $h_z = h_y$ and linear dependence around the direction. The ordering of the type $J_z(\mathbf{Q}) = -J_y(\mathbf{Q})$ will also give the same direction dependence. However, they can be distinguished when referring to the experimental result of $\Delta(z)$. The ordering of the type $J_x(\mathbf{Q}) = J_z(\mathbf{Q}) = -J_y(\mathbf{Q})$ does not have symmetry around the [111] direction. Such ordering usually does not appear. But the ordering of the type (i) can appear. Moreover, the splitting $\Delta(y)$ has different direction dependence between them.

In the ordering of type (ii), the splitting $\Delta(x)$ has the largest value for the field in the z direction. In the ordering of type (iii), the splitting $\Delta(x)$ becomes zero for $h_z/h_y = -2$, and takes a maximum at $h_y/h_z = 2$.

6. Summary

We have presented a new approach to derive the hyperfine interaction between the nuclear spin of ligand atom and multipolar moments of magnetic ions.

The most important part of this paper is the analysis on ^{17}O NMR in NpO_2 , which has been reported recently by Tokunaga et al. *et. al.*¹⁹ We have studied the ^{17}O NMR spectrum for the triple \mathbf{q} order of primary AFO and secondary AFQ, which was proposed by Paixão *et. al.*⁴ At zero field the triple \mathbf{q} AFO does not produce any hyperfine field on the O sites. However, the secondary triple \mathbf{q} AFQ order causes 4 different quadrupolar fields on the eight O sites in the fcc cube: a pair of cubic sites (with zero quadrupolar field) and 3 pairs of uniaxial-symmetry sites (the principal axis: x, y or z axis). When the magnetic field is applied, the AFM/AFO is induced in cooperation with the preexisting triple \mathbf{q} AFQ order. As a result, the NMR spectrum from the cubic site gives a sharp line with a shift proportional to the strength of the magnetic field because the hyperfine field is isotropic. On the other hand, the spectrum from three kinds of non-cubic sites gives the same shape for polycrystalline samples. Namely, it has a broadening due to the quadrupolar splitting and the magnetic field induced part caused by the anisotropic hyperfine field. The experimental observation by Tokunaga et al. is summarized as follows:

- (I) splitting to sharp and broad lines with the ratio 1:3 in the ordered phase,
- (II) the magnetic field dependence of the shift of the sharp line,
- (III) the magnetic field dependence of the width of the broad line,
- (IV) relation between the shift and the magnetic field induced part of the width.

Those features are consistently explained by our scenario. The present calculation and the experimental result in 19 strongly support to the triple \mathbf{q} ordering model of NpO_2 .

We have found theoretically that in the AFO state there are unique coupling terms such as the one causing the quadrupolar splitting proportional to the magnetic field and/or the hyperfine field splitting proportional to the square of the magnetic field. The NMR experiment for single crystals is highly desirable. On the theoretical side a microscopic calculation including the effect of finite magnetic field is desirable. In addition, although our phenomenological approach is certainly useful, a microscopic calculation of the transferred hyperfine interaction based on a microscopic model³² is also desired. Such microscopic calculations may modify quantitatively the results of the present paper, but we believe they will not change our conclusion drastically.

In the second part we have derived the hyperfine interaction between the B nuclear spin and the multipolar moments of Ce ion in CeB_6 and $\text{Ce}_{1-x}\text{La}_x\text{B}_6$. It has been applied to discuss a possibility to identify the octupolar order parameter, which was proposed for phase IV of $\text{Ce}_{1-x}\text{La}_x\text{B}_6$. We assumed the pure octupolar order of the $\Gamma_5(T^\beta)$ type with wave vector $\mathbf{Q} = \pi(1, 1, 1)$ under uniaxial stress of the $[1, 1, 1]$ direction. If it is realized in $\text{Ce}_{1-x}\text{La}_x\text{B}_6$,

the hyperfine field splitting of B nuclear spin should show characteristic features dependent on the type of order. For example, if the order of type $T_x^\beta = T_y^\beta = T_z^\beta$ occurs, the splitting $\Delta(z)$ of NMR vanishes when the direction of the magnetic field crosses the $(1\bar{1}0)$ plane. Therefore, in principle, the octupolar ordering can be identified from the direction dependence of the hyperfine splitting. Magishi *et. al.* have made an NMR experiment on the phase IV.²³ Though the observed lines are sharp enough in phase I (normal phase) , they overlap and become broad in phase IV. They speculated from the experiment that an AF magnetic ordering of incommensurate wave vector is realized. The NMR experiment under a strong uniaxial stress along $(1,1,1)$ is desirable. Although the pure AFO ordering has been assumed for phase IV, $\text{Ce}_{1-x}\text{La}_x\text{B}_6$ is actually a disordered system so that the AFO is accompanied inevitably by AFM clusters because of low local symmetry. This effect should show up in the neutron scattering experiment. In this connection we note that strange insensibility of Ce ions to the magnetic ordering in $\text{Nd}_{1-x}\text{Ce}_x\text{B}_6$ may be related to this problem.^{27,33}

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Appendix A: Derivation of Invariant Coupling Form of Hyperfine interaction in NpO_2

Let us denote the O site $(\frac{3a}{2}, \frac{3a}{2}, \frac{3a}{2})$ as ρ_1 . We consider the invariant coupling form between the nuclear spin \mathbf{I} of ^{17}O on this site and multipolar moments of f-electrons of Np ions at four nearest neighbor sites, $(2a, 2a, 2a)$, $(2a, a, a)$, $(a, 2a, a)$ and $(a, a, 2a)$ of the cube of the f.c.c. lattice. For simplicity we denote these Np ions as (111) , $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, and $(\bar{1}\bar{1}1)$, respectively. These ions have the T_d symmetry around the O atom. In a previous paper, the invariant form is derived by considering the pair interaction and rotating the pair by the symmetry operation.⁹ This method certainly gives the correct interaction form, but as noted in ref. 11, the calculation becomes relatively easier if one uses the symmetrized combination of multipolar operators. The nuclear dipole operators I_x , I_y and I_z form the 3-dimensional T_1 representation of T_d .²⁹ Following the method to make the symmetrized molecular orbital, we can construct combinations of Γ_4 , and Γ_5 and Γ_2 type odd power operators of the Np ions, which have T_1 representation.

Then, the invariant form of the hyperfine interaction of bilinear type is given as follows:

$$\begin{aligned}
 H_{\text{hf}}(\rho_1) = & I_x(\rho_1) \left[c_{1,1} \frac{1}{\sqrt{4}} \left\{ (J_x)_{(111)} + (J_x)_{(1\bar{1}\bar{1})} + (J_x)_{(\bar{1}1\bar{1})} + (J_x)_{(\bar{1}\bar{1}1)} \right\} \right. \\
 & + c_{1,2} \frac{1}{\sqrt{8}} \left\{ (J_y + J_z)_{(111)} + (-J_y - J_z)_{(1\bar{1}\bar{1})} + (-J_y + J_z)_{(\bar{1}1\bar{1})} + (J_x - J_z)_{(\bar{1}\bar{1}1)} \right\} \\
 & + c_{1,3} \frac{1}{\sqrt{8}} \left\{ (T_y^\beta - T_z^\beta)_{(111)} + (-T_y^\beta + T_z^\beta)_{(1\bar{1}\bar{1})} + (-T_y^\beta - T_z^\beta)_{(\bar{1}1\bar{1})} + (T_y^\beta + T_z^\beta)_{(\bar{1}\bar{1}1)} \right\} \\
 & + c_{1,4} \frac{1}{\sqrt{4}} \left\{ (T_{xyz})_{(111)} + (T_{xyz})_{(1\bar{1}\bar{1})} + (-T_{xyz})_{(\bar{1}1\bar{1})} + (-T_{xyz})_{(\bar{1}\bar{1}1)} \right\} \Big] \\
 & + (\text{cyclic permutation of } x, y \text{ and } z) .
 \end{aligned} \tag{A.1}$$

Here $c_{i,j}$ are the coupling constants. Next we make the Fourier transformation for multipolar operator of Np ions, $O_\gamma(\mathbf{R}_\ell) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} O_{\gamma,\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{R}_\ell}$, where \mathbf{R}_ℓ denotes the site of Np ion, and γ denotes the symmetry of the multipolar operator.

The interaction for nuclear spins at $(\frac{a}{2}, \frac{a}{2}, \frac{3a}{2})$, $(\frac{3a}{2}, \frac{a}{2}, \frac{a}{2})$ and $(\frac{a}{2}, \frac{3a}{2}, \frac{a}{2})$ can be obtained by translating the site by $(-a, -a, 0)$, $(0, -a, -a)$ and $(-a, 0, -a)$, respectively. While the interaction of nuclear spins at $(\frac{3a}{2}, \frac{3a}{2}, \frac{a}{2})$, $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$, $(\frac{3a}{2}, \frac{a}{2}, \frac{3a}{2})$ and $(\frac{a}{2}, \frac{3a}{2}, \frac{3a}{2})$ can be obtained by 90 degree rotation around z axis of the T_d and subsequent translation of the site by $(0, 0, -a)$, $(-a, -a, -a)$, $(0, -a, 0)$ and $(-a, 0, 0)$, respectively. By the rotation, the operators are changed as follows: $(I_x, I_y, I_z) \rightarrow (I_y, -I_x, I_z)$, $(J_x, J_y, J_z) \rightarrow (J_y, -J_x, J_z)$, $(T_x^\beta, T_y^\beta, T_z^\beta) \rightarrow (-T_y^\beta, T_x^\beta, -T_z^\beta)$ and $T_{xyz} \rightarrow -T_{xyz}$. The sites are changed as $(111) \rightarrow (1\bar{1}1)$, $(1\bar{1}\bar{1}) \rightarrow (11\bar{1})$, $(\bar{1}1\bar{1}) \rightarrow (\bar{1}\bar{1}1)$ and $(\bar{1}\bar{1}1) \rightarrow (1\bar{1}1)$.

The Fourier transformation is carried out in the same way as was done for eq. (A.1) of the ρ_1 site. Note that the same expression can be obtained by transforming the wave vector in the Fourier transformed equation for ρ_1 , i. e. $(q_x, q_y, q_z) \rightarrow (q_y, -q_x, q_z)$ except for the factor,

$e^{i\mathbf{q} \cdot \boldsymbol{\rho}}$. Of course, the operators are changed in the way noted above.

Appendix B: Quadrupolar coupling in NpO_2

Let us consider the quadrupolar interaction between the Γ_3 -type nuclear quadrupolar moment of O nucleus and the Γ_5 -type quadrupolar moment of Np ions,

$$\begin{aligned}
 H_{\text{qq}}(\boldsymbol{\rho}_1, c_{2,2}) &= c_{2,2} \left[O_u(\boldsymbol{\rho}_1) \frac{1}{\sqrt{4}\sqrt{6}} \left\{ (O_{yz} + O_{zx} - 2O_{xy})_{(111)} + (O_{yz} - O_{zx} + 2O_{xy})_{(\bar{1}\bar{1}\bar{1})} \right. \right. \\
 &\quad \left. \left. + (-O_{yz} + O_{zx} + 2O_{xy})_{(\bar{1}\bar{1}\bar{1})} + (-O_{yz} - O_{zx} - 2O_{xy})_{(\bar{1}\bar{1}\bar{1})} \right\} \right. \\
 &\quad \left. + O_u(\boldsymbol{\rho}_1) \frac{1}{\sqrt{4}\sqrt{2}} \left\{ (-O_{yz} + O_{zx})_{(111)} + (-O_{yz} - O_{zx})_{(\bar{1}\bar{1}\bar{1})} \right. \right. \\
 &\quad \left. \left. + (O_{yz} + O_{zx})_{(\bar{1}\bar{1}\bar{1})} + (O_{yz} - O_{zx})_{(\bar{1}\bar{1}\bar{1})} \right\} \right]. \quad (\text{B.1})
 \end{aligned}$$

Carrying out the Fourier transformation, we get

$$\begin{aligned}
 H_{\text{qq}}(\boldsymbol{\rho}_1, c_{2,2}) &= e^{i\mathbf{q} \cdot \boldsymbol{\rho}_1} c_{2,2} \frac{8}{\sqrt{4}\sqrt{6}} \left[\left\{ \frac{1}{2} (-O_u(\boldsymbol{\rho}_1) + \sqrt{3}O_v(\boldsymbol{\rho}_1)) O_{yz,\mathbf{q}} (-is_x c_y c_z + c_x s_y s_z) \right\} \right. \\
 &\quad \left. + \left\{ O_u(\boldsymbol{\rho}_1) O_{xy,\mathbf{q}} (-is_z c_x c_y + c_z s_x s_y) \right\} \right. \\
 &\quad \left. + \left\{ \frac{1}{2} (-O_u(\boldsymbol{\rho}_1) - \sqrt{3}O_v(\boldsymbol{\rho}_1)) O_{zx,\mathbf{q}} (-is_y c_z c_x + c_y s_z s_x) \right\} \right]. \quad (\text{B.2})
 \end{aligned}$$

This corresponds to the interaction term with the coupling term $c_{2,2}$ in eq. (2).

Appendix C: Derivation of Invariant Coupling Form in CeB_6

Let us consider the invariant coupling form between the nuclear spin \mathbf{I} of B on $(\frac{a}{2}, \frac{a}{2}, ua)$ and multipolar moments of f-electrons of Ce ions at (a, a, a) , $(0, a, a)$, $(0, 0, a)$ and $(a, 0, a)$ of the cube of the s.c. lattice. For simplicity we denote these Ce ions as (111) , $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}\bar{1})$, and $(1\bar{1}\bar{1})$, respectively.

These ions have the C_{4v} symmetry around the z axis. The nuclear spin operator I_z of B belongs to the A_2 representation, and (I_x, I_y) form a two-dimensional E representation.

We can construct combinations of multipolar operators of the Ce ions, which belong to A_2 and E representations. Then, the invariant form of the hyperfine interaction of bilinear type is obtained as follows:

$$\begin{aligned}
 H_{\text{hf}}(\frac{a}{2}, \frac{a}{2}, ua) &= I_z \left[c_{1,1} \frac{1}{\sqrt{4}} \left\{ (J_z)_{(111)} + (J_z)_{(\bar{1}\bar{1}\bar{1})} + (J_z)_{(\bar{1}\bar{1}\bar{1})} + (J_z)_{(1\bar{1}\bar{1})} \right\} \right. \\
 &\quad \left. + c_{1,2} \frac{1}{\sqrt{8}} \left\{ (J_x + J_y)_{(111)} + (-J_x + J_y)_{(\bar{1}\bar{1}\bar{1})} + (-J_x - J_y)_{(\bar{1}\bar{1}\bar{1})} + (J_x - J_y)_{(1\bar{1}\bar{1})} \right\} \right. \\
 &\quad \left. + c_{1,3} \frac{1}{\sqrt{8}} \left\{ (T_x^\beta - T_y^\beta)_{(111)} + (-T_x^\beta - T_y^\beta)_{(\bar{1}\bar{1}\bar{1})} + (-T_x^\beta + T_y^\beta)_{(\bar{1}\bar{1}\bar{1})} + (T_x^\beta + T_y^\beta)_{(1\bar{1}\bar{1})} \right\} \right. \\
 &\quad \left. + c_{1,4} \frac{1}{\sqrt{4}} \left\{ (T_{xyz})_{(111)} + (-T_{xyz})_{(\bar{1}\bar{1}\bar{1})} + (T_{xyz})_{(\bar{1}\bar{1}\bar{1})} + (-T_{xyz})_{(1\bar{1}\bar{1})} \right\} \right]
 \end{aligned}$$

$$\begin{aligned}
& + I_x \left[c_{2,1} \frac{1}{\sqrt{4}} \left\{ (J_x)_{(111)} + (J_x)_{(\bar{1}11)} + (J_x)_{(\bar{1}\bar{1}1)} + (J_x)_{(1\bar{1}1)} \right\} \right. \\
& + c_{2,2} \frac{1}{\sqrt{4}} \left\{ (J_z)_{(111)} + (-J_z)_{(\bar{1}11)} + (-J_z)_{(\bar{1}\bar{1}1)} + (J_z)_{(1\bar{1}1)} \right\} \\
& + c_{2,3} \frac{1}{\sqrt{4}} \left\{ (J_y)_{(111)} + (-J_y)_{(\bar{1}11)} + (J_y)_{(\bar{1}\bar{1}1)} + (-J_y)_{(1\bar{1}1)} \right\} \\
& + c_{2,4} \frac{1}{\sqrt{4}} \left\{ (T_x^\beta)_{(111)} + (T_x^\beta)_{(\bar{1}11)} + (T_x^\beta)_{(\bar{1}\bar{1}1)} + (T_x^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,5} \frac{1}{\sqrt{4}} \left\{ (-T_y^\beta)_{(111)} + (T_y^\beta)_{(\bar{1}11)} + (-T_y^\beta)_{(\bar{1}\bar{1}1)} + (T_y^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,6} \frac{1}{\sqrt{4}} \left\{ (T_z^\beta)_{(111)} + (-T_z^\beta)_{(\bar{1}11)} + (-T_z^\beta)_{(\bar{1}\bar{1}1)} + (T_z^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,7} \frac{1}{\sqrt{4}} \left\{ (T_{xyz})_{(111)} + (T_{xyz})_{(\bar{1}11)} + (-T_{xyz})_{(\bar{1}\bar{1}1)} + (-T_{xyz})_{(1\bar{1}1)} \right\} \Big] \\
& + I_y \left[c_{2,1} \frac{1}{\sqrt{4}} \left\{ (J_y)_{(111)} + (J_y)_{(\bar{1}11)} + (J_y)_{(\bar{1}\bar{1}1)} + (J_y)_{(1\bar{1}1)} \right\} \right. \\
& + c_{2,2} \frac{1}{\sqrt{4}} \left\{ (J_z)_{(111)} + (J_z)_{(\bar{1}11)} + (-J_z)_{(\bar{1}\bar{1}1)} + (-J_z)_{(1\bar{1}1)} \right\} \\
& + c_{2,3} \frac{1}{\sqrt{4}} \left\{ (J_x)_{(111)} + (-J_x)_{(\bar{1}11)} + (J_x)_{(\bar{1}\bar{1}1)} + (-J_x)_{(1\bar{1}1)} \right\} \\
& + c_{2,4} \frac{1}{\sqrt{4}} \left\{ (T_y^\beta)_{(111)} + (T_y^\beta)_{(\bar{1}11)} + (T_y^\beta)_{(\bar{1}\bar{1}1)} + (T_y^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,5} \frac{1}{\sqrt{4}} \left\{ (T_x^\beta)_{(111)} + (-T_x^\beta)_{(\bar{1}11)} + (T_x^\beta)_{(\bar{1}\bar{1}1)} + (-T_x^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,6} \frac{1}{\sqrt{4}} \left\{ (-T_z^\beta)_{(111)} + (-T_z^\beta)_{(\bar{1}11)} + (T_z^\beta)_{(\bar{1}\bar{1}1)} + (T_z^\beta)_{(1\bar{1}1)} \right\} \\
& + c_{2,7} \frac{1}{\sqrt{4}} \left\{ (T_{xyz})_{(111)} + (-T_{xyz})_{(\bar{1}11)} + (-T_{xyz})_{(\bar{1}\bar{1}1)} + (T_{xyz})_{(1\bar{1}1)} \right\} \Big] . \tag{C.1}
\end{aligned}$$

Here $c_{i,j}$ are coupling constants. By carrying out the Fourier transformation, we get the interaction form given in eq.(14).

The interaction for the nuclear spin of B on $(\frac{a}{2}, \frac{a}{2}, -ua)$ can be obtained by a mirror operation which moves B on $(\frac{a}{2}, \frac{a}{2}, ua)$ to $(\frac{a}{2}, \frac{a}{2}, -ua)$. By this transformation the multipolar operators are changed as follows: $(I_x, I_y, I_z) \rightarrow (-I_x, -I_y, I_z)$, $(J_x, J_y, J_z) \rightarrow (-J_x, -J_y, J_z)$, $(T_x^\beta, T_y^\beta, T_z^\beta) \rightarrow (-T_x^\beta, -T_y^\beta, T_z^\beta)$ and $T_{xyz} \rightarrow T_{xyz}$. At the same time, the sites are changed as $(111) \rightarrow (11\bar{1})$, $(\bar{1}11) \rightarrow (\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}1) \rightarrow (\bar{1}\bar{1}1)$, and $(1\bar{1}1) \rightarrow (1\bar{1}\bar{1})$. The Fourier transformation is carried out in the same way as was done to derive eq. (14). Note here that the same expression can be obtained by transforming the wave vector in eq. (14) as $(q_x, q_y, q_z) \rightarrow (q_x, q_y, -q_z)$ except for the factor, $e^{\frac{q_x + q_y + q_z}{2}} e^{i\mathbf{q} \cdot \boldsymbol{\rho}}$.

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p.394. The operator O_u and O_v correspond to O_0^2 and O_2^2 of ref. 2, respectively.

- 30) In the strict limit of the zero field, the level structure of the quadrupolar splitting of non-cubic sites will be equivalent though the principal axes are different with each other. Therefore there is the possibility that the quadrupolar splitting can be observed even in the polycrystalline samples.

This is pointed out by S. Kambe.

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